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SULFUR DIOXIDE OXIDATION REACTIONS IN AQUEOUS SOLUTIONS

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16. ABSTRACT

This is the final report on a three year project to study the kinetics and mechanisms of some 105 reactions involving the aqueous oxidation of sulfur dioxide and nitrogen oxides in mixed catalyst-oxidant systems at low pH (0-3). The 105 systems involve six redox reaction types: SO_2/O_2; SO_2/NO_x; SO_2/H_2O_2; SO_2/O_3; NO_x/O_3; NO_x/H_2O_2. Mn^{++} and Fe^{+++} are the only important metal catalysts. In the SO_2/NO_x system the reaction is rapid producing N_2O. The SO_2/H_2O_2 is extremely rapid and could account for the rapid formation of sulfate in the atmosphere when significant amounts of aerosol are present. The SO_2/O_3 reaction is not as rapid as the peroxide but the relative concentrations of the two makes the ozone reaction also significant.

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ABSTRACT

The kinetics and mechanisms of some 105 reactions involving the aqueous oxidation of sulfur dioxide and nitrogen oxides in mixed catalyst-oxidant systems at low pH (0-3) have been studied. The 105 systems involve six different redox reaction types: SO_2/O_2; SO_2/NO_x; SO_2/H_2O_2; SO_2/O_3; NO_x/O_3; NO_x/H_2O_2. The SO_2/O_2 system showed little reaction in the absence of catalyst. Neither was there measurable reaction in the presence of Co, Cu^{++}, VO^{++} or Pb^{++}. The SO_2/O_2 reaction, however, is catalyzed by Mn^{++} and by Fe^{+++}, with a complex synergism between Fe and Mn. A quantitative description of the synergism was developed. Synergisms were not found for Fe-Cu or Mn-Co. The iron- or manganese-catalyzed reactions were moderately inhibited by toluene, hexene, pinene, and hydroquinone, but not affected by ethanol, formaldehyde, acetic acid, or acetone.

The SO_2/NO_x system reacted rapidly with nitrite ion to produce N_2O. This reaction was not sensitive to metal ion catalysts or most organics, but did show some slight inhibition by toluene and hexene. SO_2 was unreactive to nitrate ion or dissolved NO at low pH.

The SO_2/H_2O_2 reaction was extremely fast and insensitive to catalysis or inhibition. The pH dependence and the temperature dependence of this reaction were elucidated.

The SO_2/O_3 reaction was rapid and insensitive to catalysis by metal ions or inhibition by ethanol, acetone, formaldehyde, or acetic acid.

The oxidation of nitrite ion by both ozone and hydrogen peroxide was rapid. The pH dependence of both reactions was determined.

Of these findings, the most important was the rapidity of the SO_2/H_2O_2 reaction at low pH. This reaction was fast enough to account for rapid formation of sulfate in the atmosphere when significant amounts of aerosol were present.

CONTENTS

ABSTRACT iii

1. INTRODUCTION. 1

2. CONCLUSIONS 2

3. RECOMMENDATIONS 3

4. PROCEDURES. 4

A. EXPERIMENTAL APPARATUS AND METHODS 4

1. Optical System. 4

2. Computer System 4

3. Solution Handling 6

B. DATA 7

SO_2/O_2 System. 18

SO_2/NO_x System 22

SO_2/H_2O_2 System. 23

SO_2/O_3 System. 26

NO_2^-/O_3 and NO_2^-/H_2O_2 Systems. 28

REFERENCES 29

APPENDIX A: STATUS OF PAPERS. 30

FIGURES

Number		Page
1.	Apparatus Block Diagram	1
2.	Parametric Data Fit for Fe-Mn Synergism	19
3.	Iron-Manganese Synergism Parameter	21
4.	Rate for $SO_2 + H_2O_2$ Reaction vs pH	24
5.	Rate for $SO_2 + O_3$ Reaction vs pH	27

TABLES

1.	Reaction Matrix	8
2.	Condensed Data Tabulation	10
3.	Temperature Dependence of $H_2O_2 + SO_2$ Reaction	25

1. INTRODUCTION

Air pollution by sulfur and nitrogen oxides is a major problem for society, since it is both costly to control and costly to ignore. Public awareness is growing about the problems attendant to this pollution, namely atmospheric aerosols and acid rain. Therefore, there is considerable urgency about finding cost effective ways to control these problems.

Limiting the emissions of sulfur dioxide has been only sporadically effective in controlling the sulfate and acidity levels. This may be due in part to changes in emission modes, but also seems to be due to our limited knowledge of the atmospheric chemistry that converts SO_2 to sulfate. Only three years ago, it was not possible to account for the rapidity of formation of sulfuric acid from SO_2 emissions, nor was it possible to understand the poor correlation between SO_2 and sulfate levels in the atmosphere.

As a result of recent developments in our understanding of the atmospheric chemistry, it is now possible to point to processes that can account for the rapid oxidation of SO_2. These are oxidation by OH radicals in the gas phase, and oxidation by H_2O_2 in the liquid phase of aerosols. Our preliminary calculations show that the hydrogen peroxide process can easily be the fastest route if any significant amount of aerosol is present.

This project has elucidated the kinetic behavior of the SO_2/H_2O_2 system as well as the behavior of five other redox systems of potential atmospheric importance. The kinetics were studied in a stopped-flow apparatus with UV absorption diagnostics.

2. CONCLUSIONS

The following rate expressions have been determined in this project: (all rates of formation are in moles/liter . second)

For the $SO_2 + O_2$ reaction at pH 2: (this is zeroth order in O_2)

$$d(S_{VI})/dt = 1970(Mn^{++})^2 + 82(Fe^{+++})\left(1 + \frac{2.67 \times 10^3 (Mn^{++})^{1.5}}{6.31 \times 10^{-6} + (Fe^{+++})}\right)(S_{IV})$$

For the $SO_2 + NO_2^-$ reaction:

$$d(S_{VI})/dt = 142(H^+)^{\frac{1}{2}}(HNO_2 + NO_2^-)(SO_2 \cdot Aq + HSO_3^-)$$

For the $SO_2 + H_2O_2$ reaction:

$$d(S_{VI})/dt = \frac{(8 \pm 2) \times 10^4 (H_2O_2)(SO_2 \cdot Aq)}{0.1 + (H^+)} = \frac{(5 \pm 1) \times 10^6 (HSO_3^-)(H_2O_2)(H^+)}{0.1 + (H^+)}$$

For the $SO_2 + O_3$ reaction:

$$d(S_{VI})/dt = \frac{1.9 \times 10^4 (SO_2 \cdot Aq + HSO_3^-)(O_3)}{(H^+)^{\frac{1}{2}}}$$

For the $NO_2^- + O_3$ reaction:

$$-d(O_3)/dt = \frac{200\ (O_3)(HNO_2^- + NO_2^-)}{(H^+)}$$

For the $NO_2^- + H_2O_2$ reaction:

$$-d(N_{III})/dt = 4.6 \times 10^3 (N_{III})(H_2O_2)(H^+)$$

Of these reactions, the $SO_2 + H_2O_2$ reaction is the most likely to be significant in the atmosphere when low pH aerosols are present, but any of the six reactions can become important under highly polluted conditions.

3. RECOMMENDATIONS

These recommendations for further research are based primarily on our own work, but also take into account important recent developments in the literature.

1. There should be more study about the atmospheric concentrations, sources, sinks, and side reactions of hydrogen peroxide, in view of its likely importance in the oxidation of SO_2 and NO_x.

2. Information is needed on the concentration of nitrite ion in rain and aerosols. It could form rapidly from the NO_2 + liquid water reaction, but it may also be rapidly destroyed by reactants other than SO_2.

3. Side reactions of nitrite ion need to be studied, because of the possibility of formation of toxic products.

4. The catalytic effects of suspended solids in water need to be investigated further.

5. There is still a possibility that metal ion synergisms exist in cases where one of the ions is not in itself a catalyst for the oxidation of SO_2. A number of additional combinations should be tried.

4. PROCEDURE

A. EXPERIMENTAL APPARATUS AND METHODS

1. Optical System

The apparatus used in studying aqueous reaction kinetics is shown in Figure 1. It consists of an ultraviolet light source, a stopped-flow system, a monochromator, and two different detection systems interfaced to a microcomputer.

An Oriel Model 6312 Deuterium lamp at 30-60 watts provides UV light which passes through a 2-cm optical cell contained in a Durrum D-103 stopped-flow system. The Durrum system rapidly mixes two liquid reactant solutions and allows for measuring their change in optical transmission or absorption as a function of time. It permits the observation of reaction half-times as short as two milliseconds.

The light is focused into a Princeton Applied Research 1208 Polychromator set to the desired wavelength. The disappearance of S(IV) species is monitored at 212 nm and 280 nm, the disappearance of O_3 in low pH solutions is monitored at 260 nm, and the loss of HNO_2 is monitored at 370 nm.

Two separate detection systems may be used depending on the reaction conditions. The first set-up consists of a PAR 1205D Silicon Intensified Target Detector linked to a PAR 1205A Optical Multichannel Analyzer which simultaneously measures light in a linear array of 500 channels. If necessary, the absorption at 50 different wavelengths over a 75 nm range can be monitored. This system when interfaced to the computer is used to study reaction kinetics with characteristic times slower than one second. It is necessary to change the detection system in order to study the oxidation of SO_2 by ozone or H_2O_2.

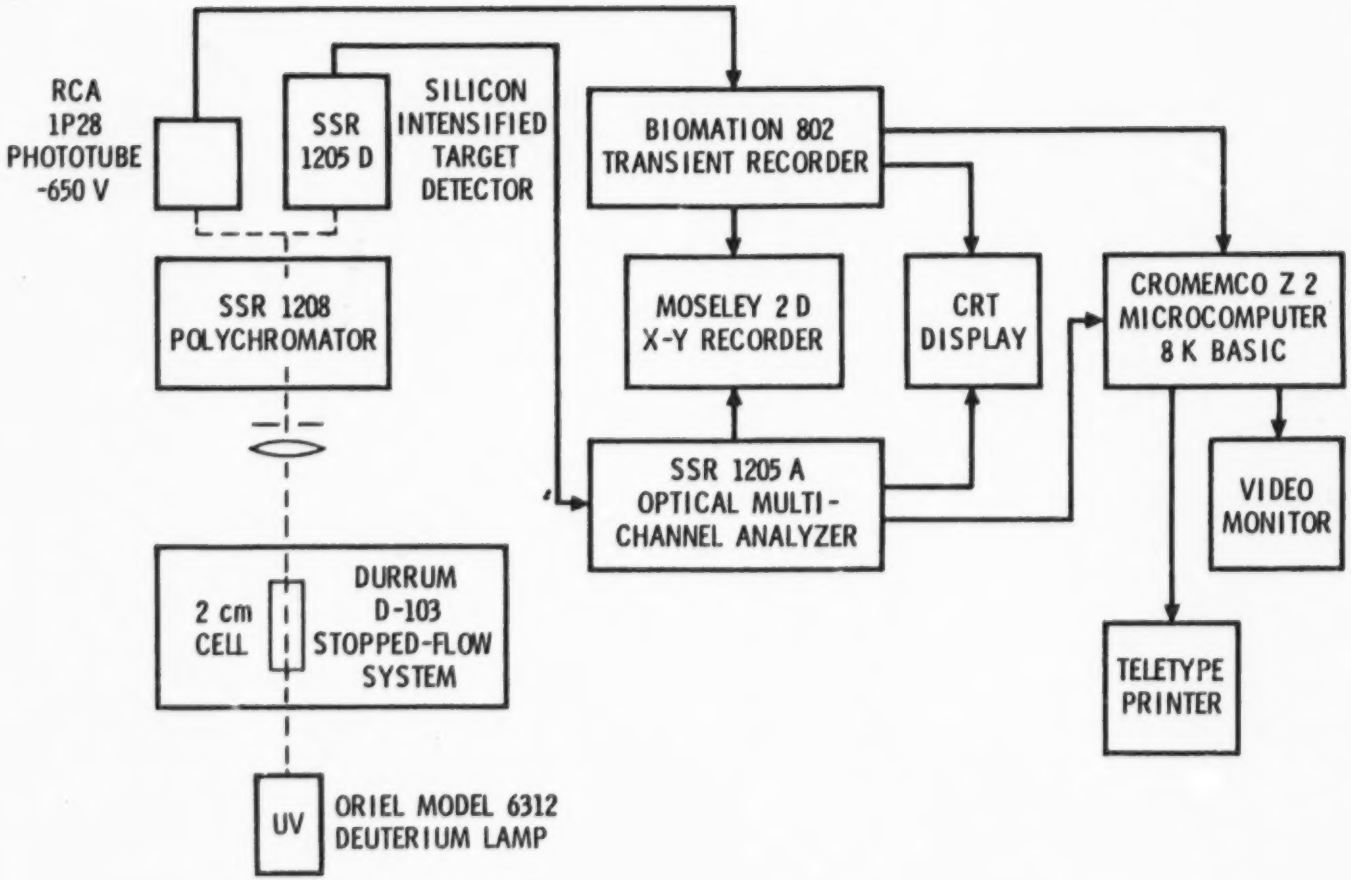

Figure 1. Apparatus Block Diagram

These reactions have half-lifes which are 1000 times faster than the O_2 reactions. The fast set-up consists of an RCA 1P28 phototube maintained at -650 V by a Fluke 405 Power Supply. The tube is linked to a Biomation 802 Transient Recorder which records a waveshape during a selected period of time and holds it in the instrument's memory until a new recording is made.

The capability exists for either detection system to be used. While the information is stored it can be viewed on an X-Y display, output to a chart recorder, and output to a computer for signal analysis and processing.

2. Computer System

The mirocomputer operates with BASIC language so that custom statements, commands, and functions can be included. It stores and processes all the data assuming Beer's Law absorption holds. A different computer program is used for the data processing depending on the detection system that is in operation. The programs are easily stored and loaded using remote-control cassette recorders interfaced to the computer. The data are output on a video monitor or teletype printer and then plotted manually to determine the kinetic rates.

3. Solution Handling

The solutions are prepared daily using 18 megohm resistivity water obtained from a Milli-Q water purification system. A pH of less than 4 is maintained using HCl as a concentration buffer. The pH of each solution is measured before reaction with an Orion 701A digital ionalyzer. The water for sulfur (IV) solutions is deoxygenated by passing a steady flow of nitrogen through it. A concentration of 10^{-3}M in dissolved oxygen for the oxidizing solution is obtainable by bubbling oxygen through the water. Ozone is produced in an ozone generator and 10^{-4}M solutions are reproducibly made by saturating the HCl solutions with 8% O_3 in O_2 from an OREC Model 03V5-0

ozonator using UHP oxygen from Matheson. The reductant is placed on one side of the stopped-flow system while the oxidant plus catalysts or inhibitors is placed on the other side. The capability exists to detect 10^{-5} M of the absorbing species but usually solutions are prepared at concentrations of 10^{-3}M to 10^{-4}M since it gives a better signal to noise ratio.

B. DATA

In Table 1 we present the complete data "matrix" in its final form. There are some minor changes from the original version, worked out mutual agreement with the EPA, which reflect the changing state of knowledge over the last three years. In the matrix, the reducing species are listed in the numbered rows, followed by two columns for catalysts or inhibitors. Five columns list oxidants or combinations of oxidants. The five oxidants are: molecular oxygen, nitrite ion (since nitrate and NO were found to be unreactive), ozone, ozone plus nitrate ion (since ozone is not compatible with nitrite or NO), and hydrogen peroxide. The matrix elements studied are indicated with a letter for cross reference to Table 2, which is a summary of the data. Table 2 gives the pH, the concentrations of reactants in the same order as the matrix, and the characteristic decay times for first order reactions or change of concentration with time for zeroth order reactions. The data given in Table 2 are average or typical data only, since the complete data list is too long for inclusion in this report. Data to determine the order of reaction are also not included to save space. The rate expressions inferred from the complete data are given in the conclusion section (Section II) of this report. A brief description of our inferences from the data follows.

Table 1 - Matrix – Final Version

Line	Reductant	Cat. I	Cat. II	Oxidant O_2	NO_2^-	O_3	$O_3+NO_3^-$	H_2O_2
1	SO_2	–	–	A	B	C	D	E
2	SO_2	–	Hexene					E
3	SO_2		Toluene					E
4	SO_2	Fe^{+3}	–	A	B	C	D	E
5	SO_2	Mn^{+2}	–	A	B	C	D	E
6	SO_2	Fe^{+3}	Mn^{+2}	A				E
7	SO_2	Fe^{+3}	Cu^{+2}	A				
8	SO_2	Pb^{+2}	–	A	B			
9	SO_2	Fe^{+3}	Co^{+2}	A				
10	SO_2	Mn^{+2}	Co^{+2}	A				
11	SO_2	VO^{+2}	–	A	B	C		
12	SO_2	Fe^{+3}	Formaldehyde	A	B	C	D	
13	SO_2	Fe^{+3}	Acetone	A	B	C	D	
14	SO_2	VO^{+2}	Acetone	A	B			
15	SO_2	Fe^{+3}	Hexene	A				E
16	SO_2	Fe^{+3}	Toluene	A				E
17	SO_2	Fe^{+3}	Pinene	A				E
18	SO_2	Mn^{+2}	Ethanol	A	B	C	D	
19	SO_2	Mn^{+2}	Formaldehyde	A	B	C	D	
20	SO_2	Mn^{+2}	Acetone	A	B	C	D	

Table 1 (Continued)

Line	Reductant	Cat. I	Cat. II	Oxidant O_2	NO_2^-	O_3	$O_3+NO_3^-$	H_2O_2
21	SO_2	Mn^{+2}	Acetic Acid	A		C	D	
22	SO_2	Mn^{+2}	Hexene	A				E
23	SO_2	Mn^{+2}	Toluene	A				E
24	SO_2	Mn^{+2}	Pinene	A				E
25	SO_2	Cu^{+2}	–	A	B	C	D	
26	SO_2	Cu^{+2}	Ethanol	A	B		D	
27	SO_2	Cu^{+2}	Formaldehyde	A	B		D	
28	SO_2	Cu^{+2}	Acetone	A	B		D	
29	SO_2	Cu^{+2}	Acetic Acid	A				
30	SO_2	Fe^{+3}	Ethanol	A	B	C	D	
31	SO_2	VO^{+2}	Ethanol	A	B			
32	SO_2	VO^{+2}	Formaldehyde	A	B	C		
33	SO_2	Fe^{+2}	Acetic Acid	A	B	C	D	
34	SO_2	VO^{+2}	Acetic Acid	A		C		
35	SO_2	Fe^{+2}	Hydroquinone	A	B			E
36	SO_2	Mn^{+2}	Hydroquinone	A	B			E
37	SO_2	Co^{+2}	–	A	B			
38	NO_2^-	–	–			C		E
39	SO_2	–	"Temperature"					E
40	SO_2	Fe, Mn	Acetone	A				

Table 2

Tabulation of Average Rates

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	Slope, M/Liter·Sec	Comments
1A	2	–	–	1×10^{-3}	$>10^5$		
1B	2	–	–	1×10^{-3} NO	>1900		Lower Limit
	0.6 to 3	None	Mn, VO, Cu, Pb, Co, Fe	2.5×10^{-3} NO_3^-	$>10^5$		
	0.6	–	–	3.0×10^{-3} NO_2^-	4.7		
	1.3	–	–	3.0×10^{-3} NO_2^-	11		
	1.5	–	–	3.0×10^{-3} NO_2^-	13		
	2	–	–	3.0×10^{-3} NO_2^-	24		
	2.5	–	–	3.0×10^{-3} NO_2^-	42		
	3.0	–	–	3.0×10^{-3} NO_2^-	74		
	2	–	–	1.5×10^{-3} NO_2^-	53		
	2	–	–	5.0×10^{-3} NO_2^-	11.5		
	2	–	–	4.0×10^{-3} NO_2^-	16.5		
1C	0.9	–	–	1.0×10^{-4} O_3	0.035		O_3 Disappearance $S_{iv} = 5 \times 10^{-4}$
	0.5	–	–	1.0×10^{-4} O_3	0.033		"
	1.6	–	–	1.0×10^{-4} O_3	0.018		"
	2.0	–	–	1.0×10^{-4} O_3	0.010		"
	2.3	–	–	1.0×10^{-4} O_3	0.008		"
	2.8	–	–	1.0×10^{-4} O_3	0.004		"
1D	1	1.5×10^{-3}	NO_3^-	1×10^{-4} O_3	0.046		O_3 Disappearance

Table 2 (Cont'd)

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	Slope, M/Liter·Sec	Comments
1 E	0.1	–	–	1.8×10^{-4}	0.120		
	0.7	–	–	4.4×10^{-4}	0.0085		
	0.8	–	–	4.4×10^{-4}	0.0115		
	1.2	–	–	4.4×10^{-4}	0.0044		
	1.5	–	–	9.0×10^{-4}	0.0023		
	2.1	–	–	1.8×10^{-4}	0.0026		
	2.2	–	–	1.8×10^{-4}	0.0027		
	2.7	–	–	3.0×10^{-3}	0.0043		
	2.8	–	–	4.4×10^{-3}	0.0036		
2 E	1.5	–	5×10^{-4}	4.4×10^{-4}	0.0042		Same as Control
3 E	1.5	–	4×10^{-5}	$4.4 \times 10^{-4} H_2O_2$	0.0059		Similar to Control
4 A	3	2×10^{-5}	–	1×10^{-3}	125		
	2	2.5×10^{-5}	–	1×10^{-3}	700		
4 B	2	2.5×10^{-5}	–	$1.5 \times 10^{-3} NO_2^-$	60		Control was 66
4 C	2	2.5×10^{-5}	–	$1 \times 10^{-4} O_3$	0.013		O_3 Disappearance
	2	5×10^{-6}	–	$1 \times 10^{-4} O_3$	0.013		"
4 D	1	2.5×10^{-5}	$1.5 \times 10^{-3} NO_3^-$	$1 \times 10^{-4} O_3$	0.040		"
4 E	1.4	2.5×10^{-5}	–	$4.4 \times 10^{-4} H_2O_2$	0.0045		Similar to Control
5 A	3	2×10^{-5}	–	10^{-3}		5.7×10^{-6} M/L·Sec	
	2	2×10^{-5}	–	10^{-3}		7.8×10^{-7} M/L·Sec	
	2	2.5×10^{-4}	–	10^{-3}		3.0×10^{-5} M/L·Sec	
5 B	2	2.5×10^{-5}	–	$1.5 \times 10^{-3} NO_3^-$	52		Control was 66
5 C	1	2.5×10^{-5}	–	$1.0 \times 10^{-4} O_3$	0.040		Looked at O_3

Table 2 (Cont'd)

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	Slope, M/Liter·Sec	Comments
5 D	1	2.5×10^{-5}	1.5×10^{-3} NO_3^-	1.0×10^{-4} O_3	0.039		Looked at O_3
5 E	1.4	2.5×10^{-5}	–	4.4×10^{-4} H_2O_2	0.0050		Similar to Control
6 A	2.1	5×10^{-7}	1×10^{-4}	10^{-3}			
	2.1	1×10^{-6}	1×10^{-4}	"		σ = 400	
	2.1	2.5×10^{-6}	1×10^{-4}	"		σ = 400	
	2.1	5×10^{-6}	1×10^{-4}	"		σ = 347	
	2.1	1×10^{-5}	1×10^{-4}	"		σ = 238	
	2.1	5×10^{-5}	1×10^{-4}	"		σ = 152	
	2.1	1×10^{-6}	5×10^{-5}	"		σ = 60	
	2.1	5×10^{-6}	5×10^{-5}	"		σ = 111	
	2.1	5×10^{-5}	5×10^{-5}	"		σ = 85	
	2.1	1×10^{-6}	2.5×10^{-5}	"		σ = 23	
	2.1	1×10^{-5}	2.5×10^{-5}	"		σ = 56	
	2.1	2.5×10^{-5}	2.5×10^{-5}	"		σ = 26	
	2.1	1×10^{-6}	1×10^{-5}	"		σ = 14	
	2.1	2.5×10^{-5}	1×10^{-5}	"		σ = 15	
	2.1	1×10^{-4}	1×10^{-5}	"		σ = 4.3	
	2.1	5×10^{-6}	5×10^{-6}	"		σ = 2.2	
	2.1	5×10^{-5}	5×10^{-6}	"		σ = 3.5	
6 E	1.4	2.5×10^{-5}	2.5×10^{-5}	4.4×10^{-4} H_2O_2	0.0056	σ = 1.8	
7 A	2.2	5×10^{-5}	5×10^{-5}	10^{-3}	400		Similar to Control
	2.2	2.5×10^{-5}	2.5×10^{-4}	10^{-3}	750		Similar to Control
8 A	3	2×10^{-5}	–	10^{-3}	$>10^4$		Similar to Control
8 B	3	2×10^{-5}	–	2.5×10^{-3} NO_3^-	$>10^4$		

Table 2 (Cont'd)

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	Slope, M/Liter·Sec	Comments
9 A	2	2.5×10^{-5}	2.5×10^{-5}	10^{-3}	650		
10 A	2	1.2×10^{-5}	1.2×10^{-5}	10^{-3}		2.2×10^{-7}	
11 A	3	2×10^{-5}	–	10^{-3}	$>10^{5}$		
11 B	2	2.5×10^{-5}	–	$1.5 \times 10^{-3} NO_2^-$	57		Control was 50
11 C	1	2.5×10^{-5}	–	$1.0 \times 10^{-4} O_3$	0.032		Looked at O_3
12 A	2	2.5×10^{-5}	5×10^{-5}	10^{-3}	600		
12 B	2	2.5×10^{-5}	5×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	58		Control was 60
12 C	1.1	2.5×10^{-5}	5×10^{-5}	$5 \times 10^{-5} O_3$	0.032		Looked at O_3
12 D	1.1	2.5×10^{-5}	5×10^{-5}	$5 \times 10^{-5} O_3$	0.032		Looked at O_3
13 A	3	2×10^{-5}	7×10^{-6}	10^{-3}	144		Control was 140
	3	2×10^{-5}	7×10^{-5}	10^{-3}	145		Control was 140
13 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	54		Control was 50
13 C	1.1	2.5×10^{-5}	7×10^{-5}	$5 \times 10^{-5} O_3$	0.034		Looked at O_3
13 D	1.1	2.5×10^{-5}	7×10^{-5}	$5 \times 10^{-5} O_3$	0.028		Looked at O_3
14 A	3	2×10^{-5}	1.4×10^{-4}	10^{-3}	$>10^{5}$		
14 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	46		Control was 50
15 A	2.2	5×10^{-4}	SAT	10^{-3}	225		Same as Control
15 E	1.5	2.5×10^{-5}	SAT	$4.4 \times 10^{-4} H_2O_2$	0.0044		Same as Control
16 A	2.2	1×10^{-5}	5×10^{-4}	$10^{-3} O_3$	4700		3X Control
	2.2	2.5×10^{-5}	5×10^{-4}	$10^{-3} O_3$	1050		2X Control
	2.2	5×10^{-5}	5×10^{-4}	$10^{-3} O_3$	280		Same as Control
16 E	1.5	2.5×10^{-5}	5×10^{-4}	$4.4 \times 10^{-4} H_2O_2$	0.0055		

Table 2 (Cont'd)

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	Slope M/Liter·Sec	Comments
17 A	2.2	2.5×10^{-5}	SAT	10^{-3}	680		
17 E	1.5	2.5×10^{-5}	SAT	$4.4 \times 10^{-4} H_2O_2$	0.0077		Same as Control
18 A	3	2×10^{-5}	7×10^{-6}	10^{-3}		3.6×10^{-6} M/L·Sec	
	2	2.5×10^{-5}	7×10^{-5}	10^{-3}		8×10^{-3} M/L·Sec	
18 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	53		
18 C	1.0	2.5×10^{-5}	8×10^{-5}	$5 \times 10^{-3} O_3$	0.035		Looked at O_3
18 D	1.0	2.5×10^{-5}	8×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.035		Looked at O_3
19 A	2	2.5×10^{-5}	5×10^{-5}	10^{-3}		1.0×10^{-6} M/L·Sec	
19 B	2	2.5×10^{-5}	5×10^{-5}	1.5×10^{-3}	55		
19 C	1.0	2.5×10^{-5}	5×10^{-5}	$5 \times 10^{-5} O_3$	0.038		Looked at O_3
19 D	1.0	2.5×10^{-5}	5×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.037		Looked at O_3
20 A	3	2×10^{-5}	7×10^{-6}	10^{-3}		4.1×10^{-6} M/L·Sec	
	2	2.5×10^{-5}	7×10^{-5}	10^{-3}		9×10^{-7} M/L·Sec	
20 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	53		
20 C	1.2	2.5×10^{-5}	7×10^{-5}	$5 \times 10^{-5} O_3$	0.038		Looked at O_3
20 D	1.2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.040		Looked at O_3
21 A	3	2×10^{-5}	1.4×10^{-5}	10^{-3}		6×10^{-6} M/L·Sec	
21 C	1.0	2.5×10^{-5}	9×10^{-5}	$5 \times 10^{-5} O_3$	0.038		Looked at O_3
21 D	1.0	2.5×10^{-5}	9×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.037		Looked at O_3
22 A	2.2	5×10^{-5}	SAT	10^{-3}		1.5×10^{-7} M/L·Sec	1/8 of Control
22 E	1.5	2.5×10^{-5}	SAT	$4.4 \times 10^{-4} H_2O_2$	0.0044		Same as Control

Table 2 (Cont'd)

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	Slope, M/Liter·Sec	Comments
23 A	2.2	1×10^{-5}	5×10^{-4}	10^{-3}		1.2×10^{-8}	1/10 of Control
	2.2	2.5×10^{-5}	5×10^{-4}	10^{-3}		4.4×10^{-8}	1/10 of Control
	2.2	5.0×10^{-5}	5×10^{-4}	10^{-3}		1.3×10^{-7}	1/7 of Control
	2.2	2.5×10^{-5}	1×10^{-3}	10^{-3}		1.7×10^{-8}	1/20 of Control
23 E	1.5	2.5×10^{-5}	5×10^{-4}	$4.4 \times 10^{-4} H_2O_2$	0.0050		Same as Control
24 A	2.2	2.5×10^{-5}	SAT	10^{-3}		5.3×10^{-8}	(70% of Control)
24 E	1.5	2.5×10^{-5}	SAT	$4.4 \times 10^{-4} H_2O_2$	0.070		Same as Control
25 A	2	2.5×10^{-5}	–	10^{-3}	$>10^5$		
25 B	2	2.5×10^{-5}	–	10^{-3}	54		
25 C	1.0	2.5×10^{-5}	–	$5 \times 10^{-5} O_3$	0.032		Looked at O_3
25 D	1.0	2.5×10^{-5}	–	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.034		Looked at O_3
26 A	2	2.5×10^{-5}	7×10^{-5}	10^{-3}	$>10^5$		
26 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	47		
26 D	1	2.5×10^{-5}	8×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.032		Looked at O_3
27 A	2	2.5×10^{-5}	5×10^{-5}	10^{-3}	$>10^5$		
27 B	2	2.5×10^{-5}	5×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	53		
27 D	1	2.5×10^{-5}	5×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.032		Looked at O_3
28 A	2	2.5×10^{-5}	7×10^{-5}	10^{-3}	$>10^5$		
28 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	56		
28 D	1	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.032		Looked at O_3
29 A	2	2.5×10^{-5}	5×10^{-5}	10^{-3}	$>10^5$		
30 A	3	2×10^{-5}	7×10^{-6}	10^{-3}	150		Control was 135
	2	2.5×10^{-5}	7×10^{-5}	10^{-3}	1000		Control was 900
30 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	60		

Table 2 (Cont'd)

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	Slope, M/Liter·Sec	Comments
30 C	1.0	2.5×10^{-5}	8×10^{-5}	$5 \times 10^{-5} O_3$	0.034		Looked at O_3
30 D	1.0	2.5×10^{-5}	8×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.034		"
31 A	2	2.5×10^{-5}	7×10^{-5}	10^{-3}	$>10^4$		
31 B	2	2.5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	59		
32 A	2	2.5×10^{-5}	5×10^{-5}	10^{-3}	$>10^4$		
32 B	2	2.5×10^{-5}	5×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	54		
32 C	1	2.5×10^{-5}	5×10^{-5}	$5 \times 10^{-5} O_3$	0.034		Looked at O_3
33 A	3	2×10^{-5}	1.4×10^{-5}	10^{-3}	113		Control was 86
	2	5×10^{-5}	7×10^{-5}	10^{-3}	350		
33 B	2	5×10^{-5}	7×10^{-5}	$1.5 \times 10^{-3} NO_2^-$	48		
33 C	1.0	2.5×10^{-5}	9×10^{-5}	$5 \times 10^{-5} O_3$	0.028		
33 D	1.0	2.5×10^{-5}	9×10^{-5}	$1.5 \times 10^{-3} NO_3^- \; 5 \times 10^{-5} O_3$	0.034		
34 A	2	2.5×10^{-5}	7×10^{-5}	10^{-3}	$>10^4$		
34 C	1	2.5×10^{-5}	9×10^{-5}	$5 \times 10^{-5} O_3$	0.034		Looked at O_3
35 A	2.2	2.5×10^{-5}	5×10^{-6}	10^{-3}	10,000		Inhibition
	2.2	5×10^{-5}	5×10^{-7}	10^{-3}	240		No Effect
35 B	2.2	2.5×10^{-5}	5×10^{-7}	$1.5 \times 10^{-3} NO_2^-$	70		
35 E	1.5	2.5×10^{-5}	5×10^{-6}	$4.4 \times 10^{-4} H_2C_2$	0.0066		Same as Control
36 A	2.2	2.5×10^{-5}	5×10^{-6}	10^{-3}		4.5×10^{-8}	Inhibition
36 B	2.2	2.5×10^{-5}	5×10^{-7}	$1.5 \times 10^{-3} NO_2^-$	69		
36 E	1.5	2.5×10^{-5}	5×10^{-6}	$4.4 \times 10^{-4} H_2O_2$	0.0066		Same as Control

Table 2 (Cont'd)

Matrix Element	pH	Cat. I Concentration	Cat. II Concentration	Oxidant Concentration	τ, Sec	M/Liter·Sec	Comments
37 A	2	2.5×10^{-5}	–	10^{-3}	$>10^4$		
37 B	3	2×10^{-5}	–	$2.5 \times 10^{-3} NO_3^-$	$>10^4$		
38 C	1.0	$2.5 \times 10^{-4} NO_2^-$	–	$5 \times 10^{-5} O_3$	2.0		
	1.6	"	–	"	0.50		
	2.2	"	–	"	0.126		
	2.8	"	–	"	0.038		
	3.6	"	–	"	0.005		
	2.8	$5 \times 10^{-4} NO_2^-$	–	"	0.014		
	2.8	$1 \times 10^{-4} NO_2^-$	–	"	0.080		
	2.8	$1.5 \times 10^{-3} NO_2^-$	–	"	0.004		
38 E	1.3	$1.5 \times 10^{-3} NO_2^-$	–	$4.4 \times 10^{-3} H_2O_2$	0.94		
	2.1	"	–		5.5		
	3.4	"	–		128		
	3.8	"	–		630		
39 E	2.3	24°C	–	$8.5 \times 10^{-4} H_2O_2$	0.0055		
	2.3	15°C	–	"	0.0087		
	2.3	5°C	–	"	0.0116		
40 A	3	Fe, Mn	–				
		2×10^{-5}	7×10^{-6}	10^{-3}	225		Control was 160

SO_2/O_2 System

With our ultrapure water and in the absence of added catalysts, this reaction does not occur at a measurable rate ($\tau > 10^5$ sec) at low pH (0-3). The cations VO^{++}, Pb^{++}, Cu^{++}, or Co^{++} also do not cause reaction at low pH. Fe^{+++} catalyzes a first order oxidation of S_{IV}, and Mn^{++} catalyzes a zeroth order oxidation of S_{IV}. The Fe^{+++} catalyzed reaction is first order in iron, and the Mn^{++} catalyzed reaction is second order in Mn^{++} becoming first order as the manganese concentration approaches the sulfur concentration. Both the iron and manganese systems are insensitive to the presence of acetone, formaldehyde, acetic acid (at constant pH), or ethanol. Toluene or hexene at concentrations of 10^{-3} molar slow the iron system by a factor of about 3, and the manganese system by a factor of about 10. The manganese system appears to have half-order dependence on the toluene concentration. Similar but smaller inhibitions were seen for pinene and hydroquinone, so double bonds correlate with the effect.

Iron and manganese exhibit a catalytic synergism that we studied in detail, and we now have a quantitative picture of how it works. The iron-manganese system is complicated by the fact that the iron catalyzed system obeys first order kinetics in sulfur (IV) and the manganese catalyzed system obeys zeroth order kinetics in sulfur (IV). Thus, one would expect that the combined system would exhibit a more complex behavior described by the differential equation:

$$d(S_{IV})/dt = -a - b(S_{IV})$$

In fact, the reaction rate of the mixed catalyst system is faster than this equation would indicate. Our first discovery about the synergism was that the rate enhancement may be attributed to an increase in the first order term only. This is illustrated in Figure 2, which shows the decay of reduced

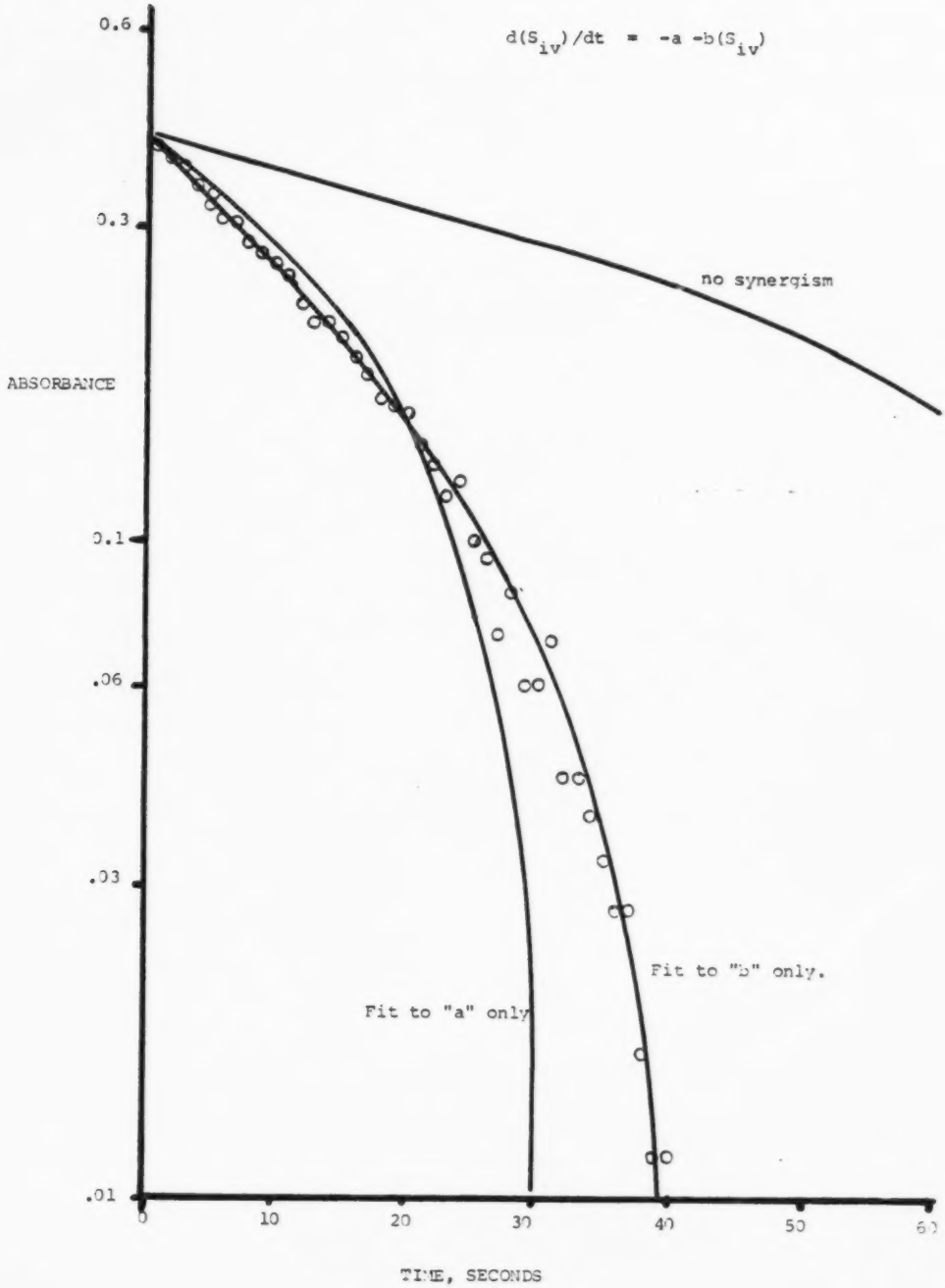

Figure 2 Parametric Data Fit

sulfur with time for a system at pH 2 containing 1×10^{-4} M manganese and 2.5×10^{-6} M iron. The three curves drawn are for no synergism, i.e., for a linear combination of the rate constants in the separate systems; for a fit to the first order term only at 20 seconds (1/e time); and for a fit to the zeroth order term only at 20 seconds. It is clear that the fit to the first order term is the best fit, and that it describes the data very well. This was true for data taken over a wide range of concentrations of both catalysts. For the data in Figure 2, the curve is drawn for a parameter sigma equal to 347 in the expression:

$$d(S_{IV})/dt = -a - b\sigma(S_{IV})$$

Having found a parameter that describes the synergism and the rate behavior for mixed systems, we next determined the dependence of the parameter sigma on the two concentrations of catalyst. This dependence is shown by the family of curves in Figure 3. The complete behavior of the system at pH 2 is described by the expression:

$$d(SO_4^{=})/dt = 1970(Mn^{++})^2 + 82(Fe^{+++}) \left\{ 1 + \frac{2.67 \times 10^3 (Mn^{++})^{1.5}}{6.31 \times 10^{-6} + (Fe^{+++})} \right\} (S_{IV})$$

This expression means that manganese catalyzes the first order iron catalyzed reaction with the result that the first order reaction may be hundreds of times faster than one would expect from the iron concentration alone. Nevertheless, the overall rates are typically only three to ten times faster than one would expect for iron-manganese concentrations typically found in aerosols. The synergism was found not to be sensitive to the presence of acetone.

We looked also for possible synergisms between Fe-Co, Mn-Co, and Fe-Cu, but found none.

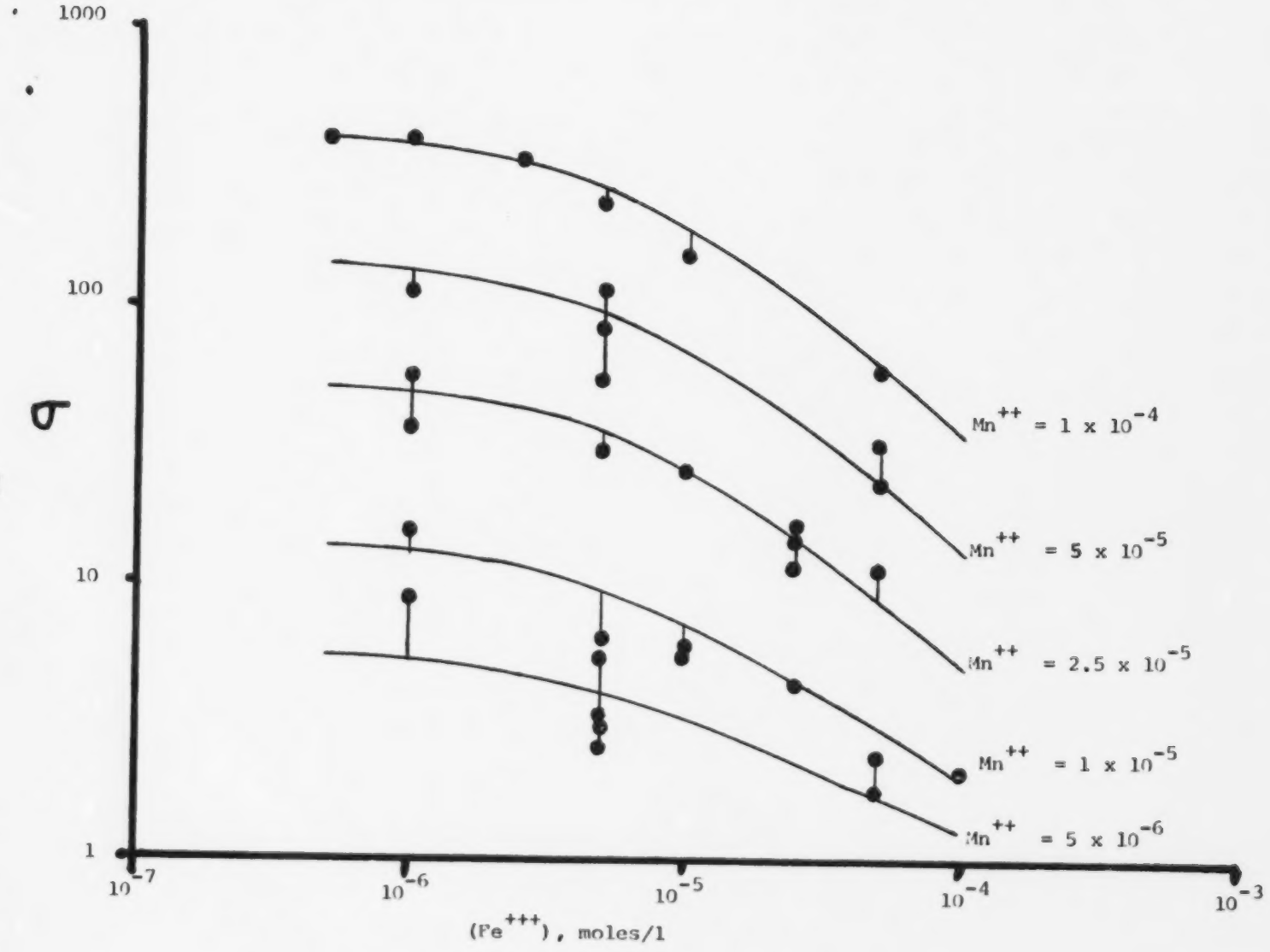

Figure 3 Iron-Manganese Synergism Parameter

SO_2/NO_x System.

The aqueous nitrogen species likely to be present in the atmosphere are NO_2^-, NO_3^-, and dissolved NO. If other hydrated oxides exist in solution, their concentrations may be related to the concentrations of these three species by equilibrium constants. We studied pure preparations of each of the three. Nitric acid/nitrate ion was found to be unreactive to sulfur (IV) in solution, even at pH values as low as 0.5. The ions Fe^{+++}, Mn^{++}, Cu^{++}, Co^{++}, Pb^{++}, and VO^{++} were all run with nitrate/SO_2 and none catalyzed the reaction.

Dissolved NO was difficult to prepare, since the gas often contains NO_2 as an impurity. Highly purified NO in deoxygenated water was not reactive with sulfur (IV). Thus, for both nitrate and dissolved NO gas at low pH (≤ 3)

$$d(S_{IV})/dt \leq -0.01(NO_x)(S_{IV}) \text{ moles/l} \cdot \text{sec}$$

Nitrite ion, on the other hand, reacts rapidly with sulfur (IV), with a rate expression given in Section II of this report. This reaction is not catalyzed by Fe^{+++}, Mn^{++}, or VO^{++}. The reaction is inhibited about six-fold by hexene. This inhibition was the only example we found of a "fast" reaction sensitivity to other reagents.

The nitrite reaction has the interesting feature that the reaction product below pH 3 is nitrous oxide, N_2O. Our preliminary estimates of the global source strength indicate that this will not be an important source of N_2O, however. The nitrite-sulfur (IV) reaction is also not very fast in unpolluted air, but might be important in high NO_x pollution situations. Details about this system are given in our paper referenced in the Appendix.

SO_2/H_2O_2 System

Hydrogen peroxide was added to our matrix when the high pH data of Penkett, et. al. [1], and the peroxide environmental measurements of Kok, et. al. [2] indicated that this could be an important reaction in atmospheric aerosols. Our data at low pH showed that this reaction is faster than one would expect from a straight extrapolation of the high pH data. A plot of our data and the data of others is given in Figure 4, which is a plot of the rate constant k_o in the expression:

$$d(S_{VI})/dt = k_o(H_2O_2)(S_{IV})$$

The solid curve in this figure is the rate expression given in the Conclusions section of this report (Section II). The dashed part of the curve includes a high pH term from the literature. We found that this expression could be fit to a mechanism suggested by Hoffmann and Edwards [3] for this system.

The peroxide reaction was found to be insensitive to catalysis or inhibition by Fe^{+++}, Mn^{++}, hydroquinone, toluene, pinene, or hexene. We also did a temperature dependence of this reaction rate, and these data are summarized in Table 3.

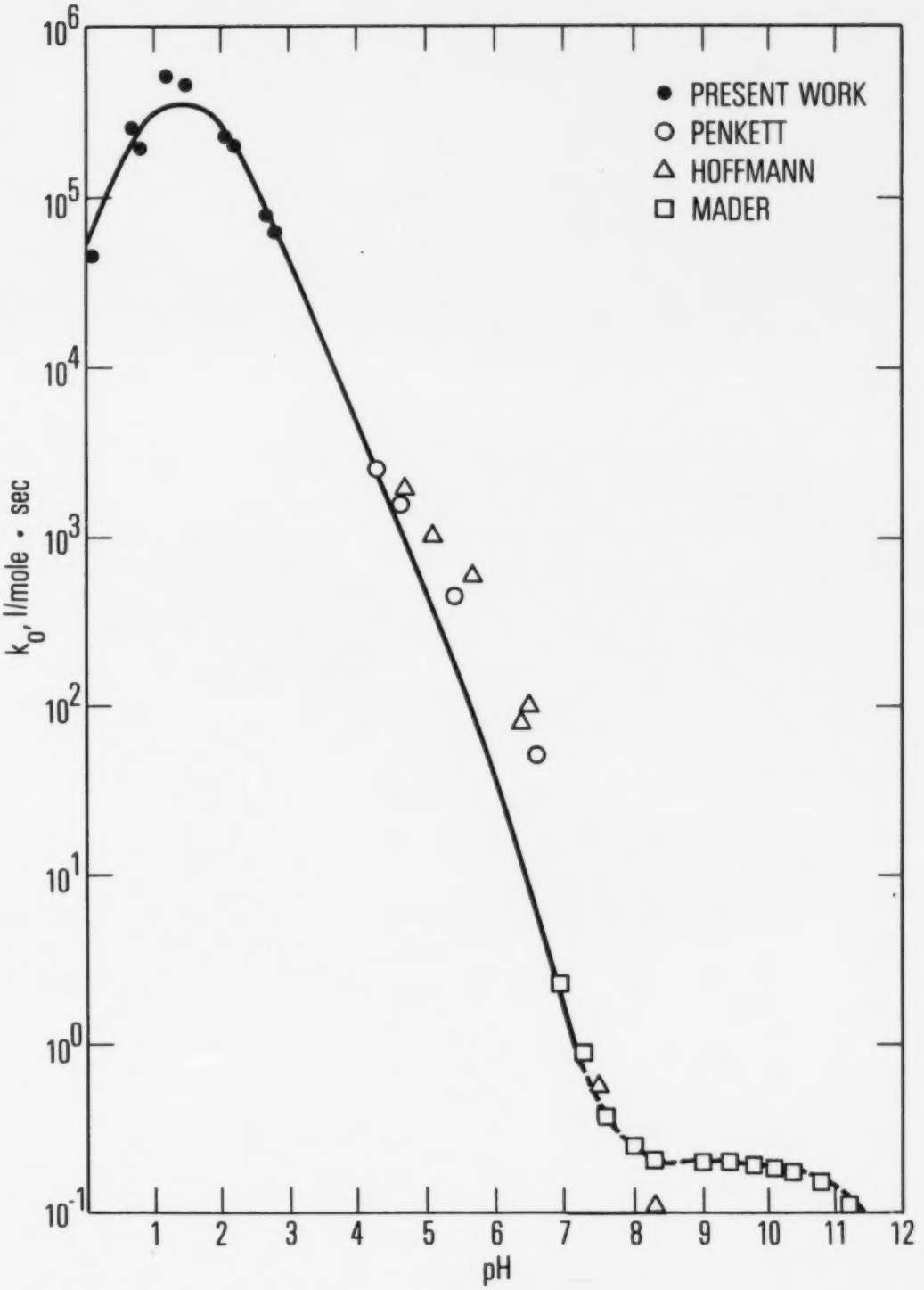

Figure 4. k_0 in Expression $d(S_{VI})/dt = k_0 (H_2O_2) (S_{IV})$. Effect of Buffer Removed - Results Converted to 25 Celsius

Table 3

Temperature Dependence of Peroxide - SO_2 Reaction

TEMP., CELSIUS	K_H, SO_2	K_H, H_2O_2	NORMALIZED RATE CONSTANT	NORMALIZED PRODUCT
25	1.23	7.1×10^4	1.000	1.000
20	1.45	1.1×10^5	0.82	1.4
15	1.76	1.7×10^5	0.67	2.2
10	2.20	2.5×10^5	0.55	3.4
5	2.69	3.8×10^5	0.44	5.2
0	3.28	6.1×10^5	0.35	8.0

In the table, the kinetic rate is given in the fourth column, normalized to unity at 25 Celsius. The rate in the atmosphere will also depend on the Henry's Law constants for SO_2 and H_2O_2, and these are given in the second and third columns, respectively. The fifth column gives the net rate in an atmospheric aerosol normalized to unity at 25 Celsius, assuming that all other quantities remain equal. It can be seen from the table that the relatively low activation energy for the kinetics leads to a net increase in the atmospheric rate as the temperature is lowered because of the rising Henry's Law constants.

Our estimates of the atmospheric oxidation rate for 1ppb of hydrogen peroxide in the gas phase and in a typical cloud are on the order of 2% per minute for SO_2, which is higher than any reported rates, and about as high as the rate allowed by the heterogeneous reactivity of SO_2 with the droplet surfaces. Details about this system are given in our paper referenced in the Appendix.

SO_2/O_3 System.

Our data for this system are compared with those in the literature in Figure 5. It can be seen that we are in essential agreement with most of the previous work. The rate expression for this reaction is given in Section II of this report. This rate was found to be insensitive to the presence of Fe^{+++}, Mn^{++}, VO^{++}, Cu^{++}, as well as various combinations of these ions with formaldehyde, acetone, acetic acid, and ethanol. Adding nitrate to these systems also did not affect the rate. Organics containing double bonds were not tested because of the difficulties associated with the cross reaction with ozone. There is still a possibility that such systems react faster than pure ozone in analogy to the gas phase kinetics.

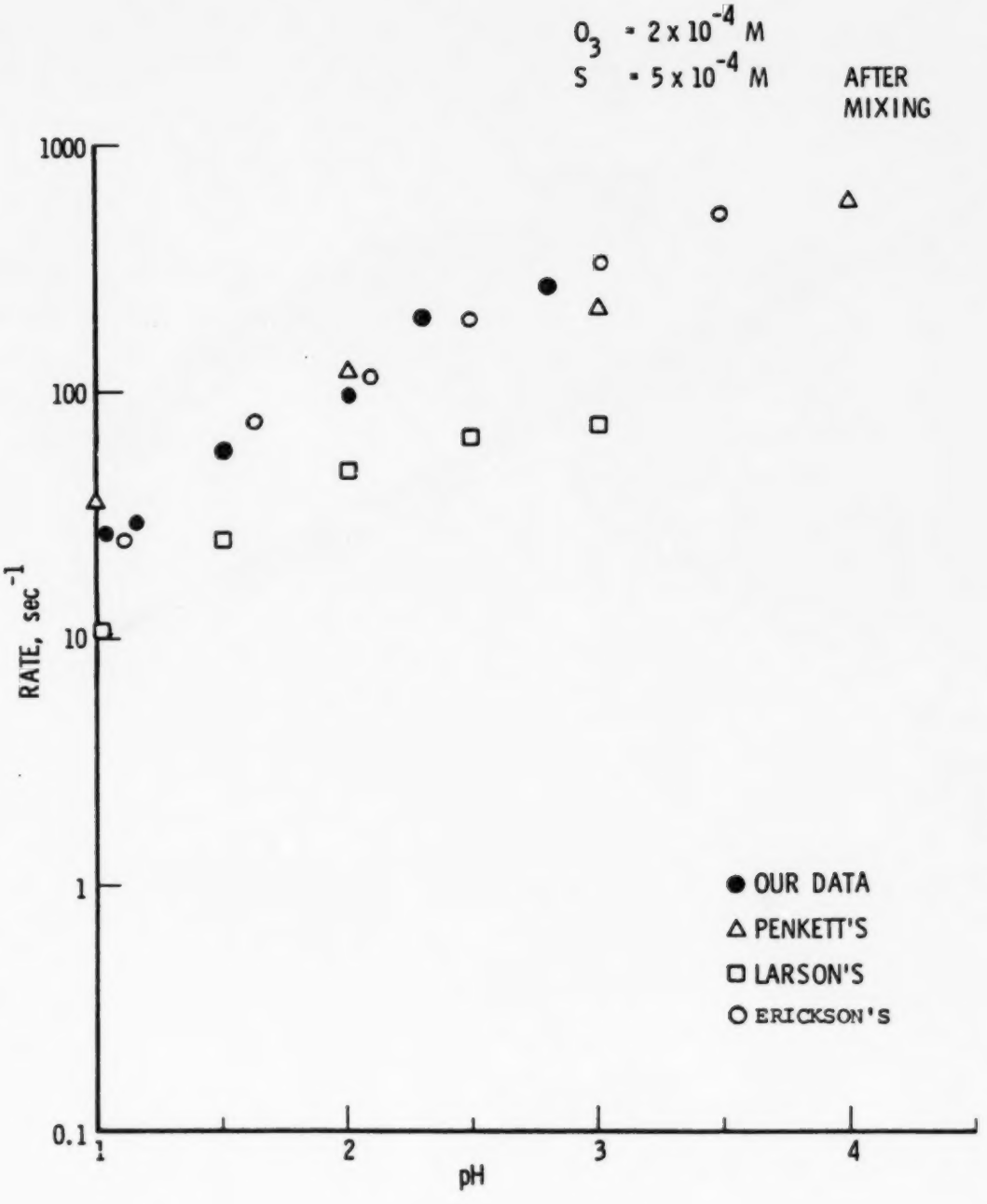

Figure 5 SO_2-Ozone pH Dependence

NO_2^-/O_3 and NO_2^-/H_2O_2 Systems.

The pH dependence of these two systems was determined and is given in the rate expressions in the Conclusions Section. The rates are moderately fast, but are about three orders of magnitude slower than the corresponding SO_2 reactions at pH 1. Thus, NO_x is unlikely to compete with SO_x for these oxidants, but the reactions may be important for the NO_x cycle if no faster reactions are found. The products and catalytic sensitivities of these reactions were not determined.

REFERENCES

1. S. A. Penkett, et. al., Atmospheric Environment, 13 123-127 (1979).
2. G. L. Kok, et. al., Environ. Sci. Technol. 12, 1077-1080 (1978).
3. M. R. Koffmann and J. O. Edward, J. Phys. Chem. 79, 2096-2098.

APPENDIX A: STATUS OF PAPERS

In Press.

"The Reactions of Nitrogen Oxides with SO_2 in Aqueous Aerosols" by L. Robbin Martin, Donald E. Damschen, and Henry S. Judeikis, Atmospheric Environment, 1981.

"Aqueous Oxidation of Sulfur Dioxide by Hydrogen Peroxide at Low PH" by L. Robbin Martin and Donald E. Damchen
Atmospheric Environment

In Preparation.

1. Paper on the iron-manganese synergism
2. Paper on the effects of organics
3. Paper on the nitrite reactions.